

Electronic Supplementary Material

An interfacial polymerization strategy towards high-performance flexible supercapacitors

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Experimental Section

Materials: TPU and PEDOT film was bought from Wiman company. EDOT monomer and FeCl₃ were got from Sigma-Aldrich Co., Ltd. Ionic liquid was obtained from Sinopharm Chemical Reagent Co., Ltd. Deionized water was homemade.

Preparation of supercapacitors with interfacial polymerization strategy: Firstly, TPU film was soaked into EDOT for 1 h and then the surface was wiped off with filter paper. After that, the swollen film was immersed into FeCl₃ solution with concentration of 1.5 mol L⁻¹ for 0.5 h. Subsequently, the film surface was washed 3 times with methanol and dried at 60 °C under vacuum for 24 h. Lastly, the supercapacitor was obtained by immersing into ionic liquid for 12 h.

Preparation of supercapacitors with conventional hot pressing method: Firstly, one layer of TPU film was laminated with two layers of PEDOT films. Then, the three layers were assembled together through hot pressing method. Lastly, the supercapacitor was got by soaking into ionic liquid after 12 h.

Material Characterizations: SEM characterization was measured by Hitachi S-4800 equipment. Flexibility performances were studied using universal tester (Shimadzu, AGS-X) and motorized translation stages (MTS121). Electrochemical properties of supercapacitor were measured through Biological electrochemical systems.

Additional Fig.s and Results

Most researches in the field of supercapacitors focus on design and synthesis of novel electrode nanomaterials for the purpose of achieving higher energy storage capacity. This is mainly because nanomaterials, including graphene,¹ carbon nanotube² and MXene,³ have potential for improving ion accommodation and transferring electrons in electrodes during electrochemical processes owing to the special nanostructure characteristics, such as high specific surface area, porous structure, abundant active sites and high conductivity.⁴ But less attention has been paid to interface between electrodes and electrolyte in all-solid-state supercapacitors, which is critical to applications in flexible conditions.⁵ Because interfaces of supercapacitors prepared from conventional hot-pressing method are fragile and easy to break under applied forces in flexible conditions, which hinder development of flexible supercapacitors.⁶ In this work, an interfacial polymerization strategy for fabricating robust interface in supercapacitor is firstly put forward. The as-prepared flexible supercapacitor gives stable energy capacity during charge-discharge cyclings under twisted and bending conditions over more than 2500 cycles, which was significantly higher than that of the device based on conventional method. Thus this strategy represents new insight into the design of robust interfaces with superior mechanical endurance properties and will accelerate application of flexible supercapacitors.

Many studies on nanomaterial electrode for supercapacitors, including graphitic carbon nitride,⁷ graphene⁸ and graphdiyne⁹, show higher energy storage capacity and fine rate performances because of the improved electrochemical dynamics. But these all-solid-state devices present limited performance under flexible conditions and some reported works on flexible supercapacitors show stable energy supply under bending state with charge-discharge cycles less than 500 times.^{6, 10} In this work, flexible supercapacitor with robust interface could keep working stably after 2500 cycles, which indicates the importance of interface in the device. As the electrode material used in this work is polymer lacking structure characteristics of nanomaterials, the energy storage capacity is lower than nanomaterials based devices. In future works, we will combine the interface strategy with nanomaterials to achieve flexible supercapacitors

with both mechanical and electrochemical properties.

Conventional assembly method involves with hot-pressing of PEDOT electrode layers and TPU polyelectrolyte layer. This kind of devices will encounter delamination under flexible conditions between electrode and electrolyte layers because of modulus mismatch of the two layers and weak adhesion force between them.^{11, 12} But the interfacial method in this work makes polymerization of electrode layers on and near surface of TPU matrix, which could form robust interfacial transition layers composed of PEDOT and TPU polymers, as shown in sulfur EDX mapping of cross section of the device in Fig. 2c. PEDOT and TPU polymers in the interfacial transition layers mainly form tangled polymer chains rather than chemical bond because FeCl_3 agent for EDOT polymerization is a weak initiator and will not active groups of TPU to form chemical reactions with PEDOT.^{13, 14} The tangled interfacial transition layer between electrode and electrolyte avoids modulus mismatch and adhesion issues and thus gives better flexible performances.

In this work, FeCl_3 is applied as oxidant for polymerization as well as dopant for PEDOT. Thus the dopants in the oxidatively polymerized PEDOT film is FeCl_4^- and Cl^- .^{13, 15} Conductivity of the as polymerized PEDOT is 764 S cm^{-1} , which is slightly lower than the PEDOT film on graphene surface (782 S cm^{-1}) prepared from its aqueous solution. There is no extra current collector used in this work because conductivity of PEDOT electrode film is high enough for electron collection and its good mechanical properties guarantee stable energy supply under flexible conditions. And hard current collectors should be avoided because of modulus mismatch of different layers and their weak interfaces, which will lead to delamination between different layers in device under mechanical deformations.

In future works, we will focus on updated and new progresses on flexible supercapacitors, especially researches on design and synthesis of nanomaterials (black phosphorus, $\text{g-C}_3\text{N}_4$ and MXene), novel fabrication methods (in-situ synthesis and microfluidic methods) and fiber shaped supercapacitors (from micro to nanoscale level). We intend to combine the interface strategy in this work with novel structure electrode materials and one-dimensional fiber shaped devices with purpose of

developing supercapacitors with both high energy storage capacity and mechanical properties for practical applications. And we will also consider to design novel structure nanomaterials with robust interface coupling effect with polyelectrolyte and also intend to develop artificial interface layers with fine mechanical properties and ionic conductivity for flexible supercapacitors. And more, theoretical/simulation methods will be applied to evaluate the energy storage mechanism behind the experimental phenomena, such as finite element model and density functional theory.

In order to verify that there is no interface dislocation happening, we prepared three cross-sectional samples of the supercapacitors under different bending degrees on the SEM stage. Schematic diagram of the setup with marked area is shown in Fig. S6a. Cross-sectional SEM images of devices under different bending degrees are presented in Fig. S6b-d. It is clearly found that there exists no obvious interface dislocation under flexible conditions with bending degrees from 0 to 180°.

SEM image in Fig. 1e presented the smooth and dense surface morphology of PEDOT electrode with high quality formed through interfacial polymerization strategy. It is possible to construct a non-uniform PEDOT electrode to study the influence on holistic conductivity. As we known, PEDOT aqueous solution can not be spread uniformly onto hydrophobic surface like graphene because of the high polarity of water molecules. And isopropyl alcohol (IPA) was introduced to reduce the polarity of PEDOT solution for uniform spreading on graphene surface. Based on this theory, we prepared two samples of PEDOT films on graphene films, including uniform one with IPA regulation (mass ratio of IPA/PEDOT solution=1:1) and non-uniform one with the aqueous solution. SEM images of the two samples are presented in Fig. S7. It is found that IPA regulated sample shows uniform morphology while the other one displays non-uniform morphology. Then, conductivities of the two PEDOT electrodes were measured by multifunction digital four-probe tester and the uniform sample displays higher conductivity (314 S cm^{-1}) than that of non-uniform one (782 S cm^{-1}).

In order to demonstrate the enhanced mechanical property of in-situ polymerized device, shear tests of two devices prepared with interfacial polymerization and conventional assembly methods were conducted under different stress. The schematic

for shear test of devices is shown in Fig. S8a and the capacitance retention of the devices as function of stress is presented in Fig. S8b. Capacitance of supercapacitors both degraded with increasing of shear stress, but the capacity of conventional assembly device only kept less than 20% of initial state while that of interfacial polymerization sample still kept at 72%. This result indicates the enhanced mechanical property of device prepared with interfacial polymerization strategy and the shear stress endurance of device could be further improved by increasing its thickness in future works.

In order to identify this result clearly, an enlarged selected area of SEM sulfur mapping image in Fig. 2c was provided in Fig. S9d. In this characterization, sulfur mapping was applied because there is sulfur element in PEDOT networks but there is not any sulfur in TPU networks. Therefore, PEDOT distribution in the interface of supercapacitors can be traced according to sulfur mapping result. It can be found in Fig. S9d that PEDOT layer is above the boundary line marked in yellow and the PEDOT/TPU transition layer with gradient distribution of PEDOT polymers is under the boundary line. This result is also illustrated in cross-section schematic in Fig. 2a and the corresponding cross-sectional SEM image of supercapacitor is provided in Fig. 2b.

There is no sealing measures for devices. On one hand, numerous carbamate groups in the structure of thermal polyurethane not only absorbed high-loading of ionic liquid, but also keep the ionic liquid in polymer matrix without massive leakage in air. On the other hand, the TPU/EMITFSI electrolyte layer is laminated with two compact PEDOT electrode layers. Thus the device could be kept stable in air without sealing measures. We also test charge-discharge performance of the device after exposing in air for 86 days in Fig. S10 and there is negligible performance degradation compared with the initial device.

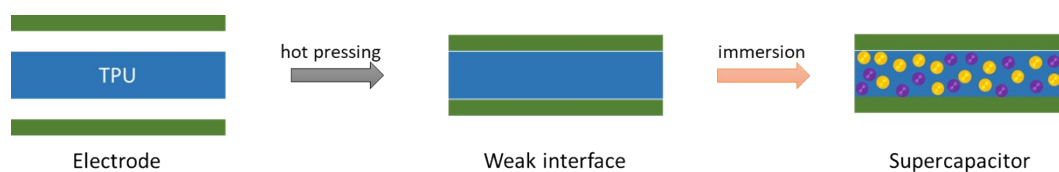


Fig. S1 Schematic for the fabrication of supercapacitors based on conventional method.

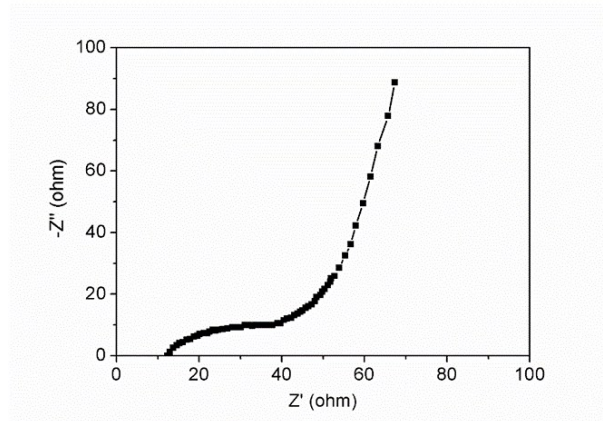


Fig. S2 Nyquist plot for the device based on conventional method.

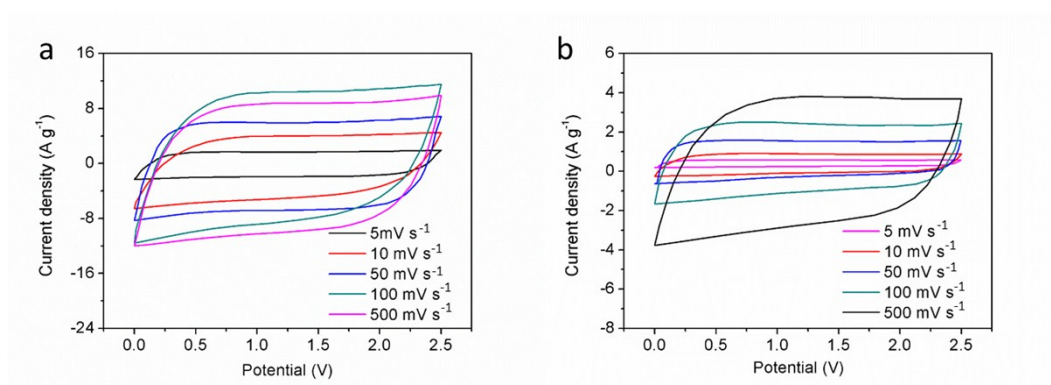


Fig. S3 CV curves of the devices based on interfacial strategy (a) and conventional method (b) under various scan rates, respectively.

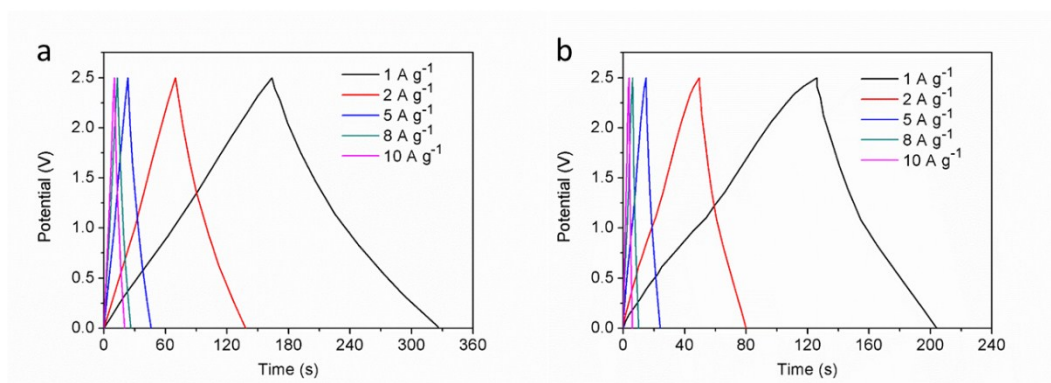


Fig. S4 CD curves of the devices based on interfacial strategy (a) and conventional method (b) under various current densities, respectively.

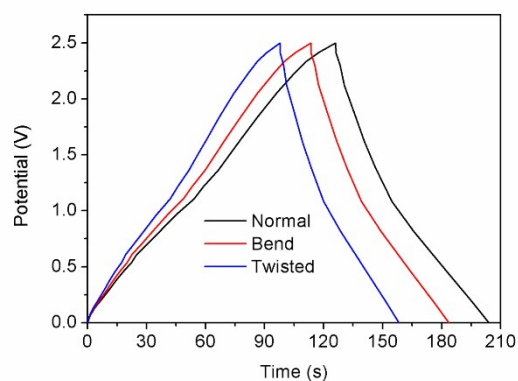


Fig. S5 CD curves of the device based on conventional method under normal, bend and twisted states.

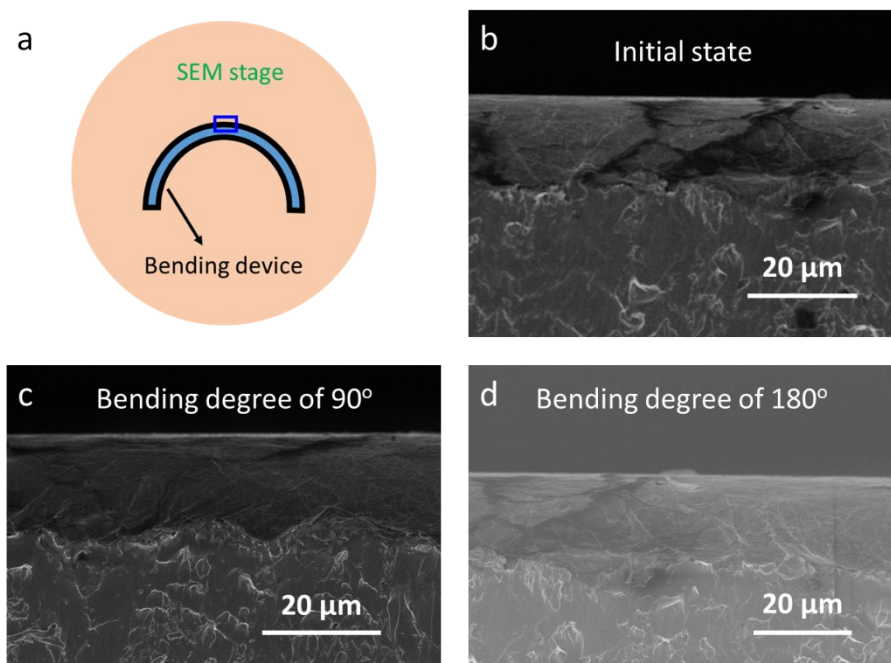


Fig. S6 (a) Schematic diagram of the setup with marked area. (b-d) Cross-sectional SEM images of supercapacitors in selected area under bending degrees of 0, 90° and 180°, respectively.

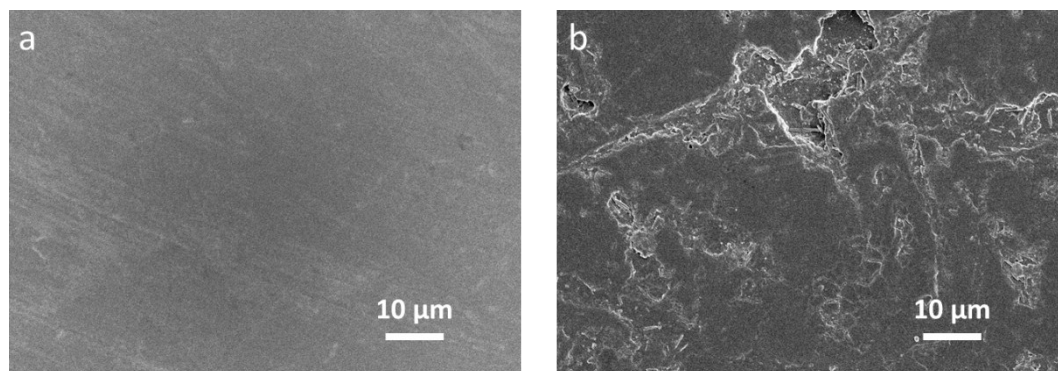


Fig. S7 Surface SEM images of (a) IPA regulated (uniform) and (b) non-regulated (non-

uniform) PEDOT electrodes.

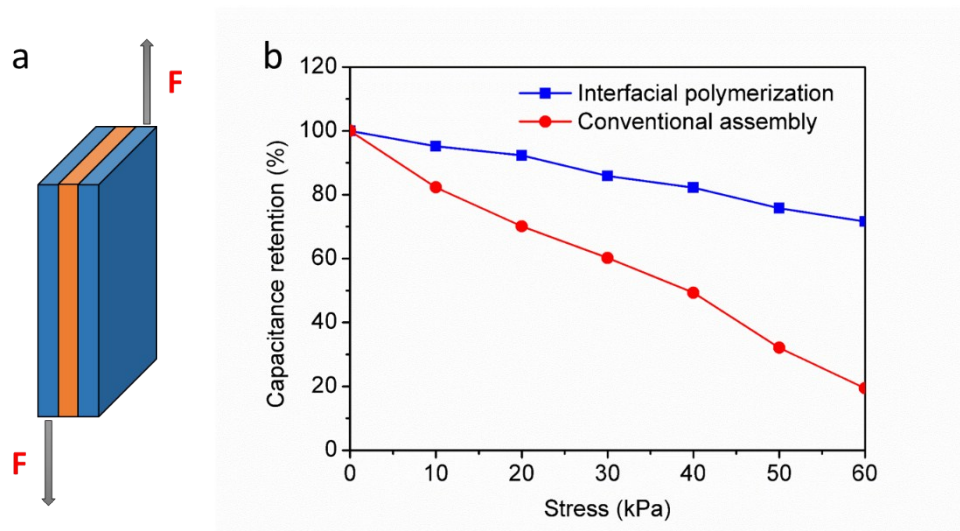


Fig. S8 (a) Schematic for shear test. (b) capacitance retention of the devices as function of stress.

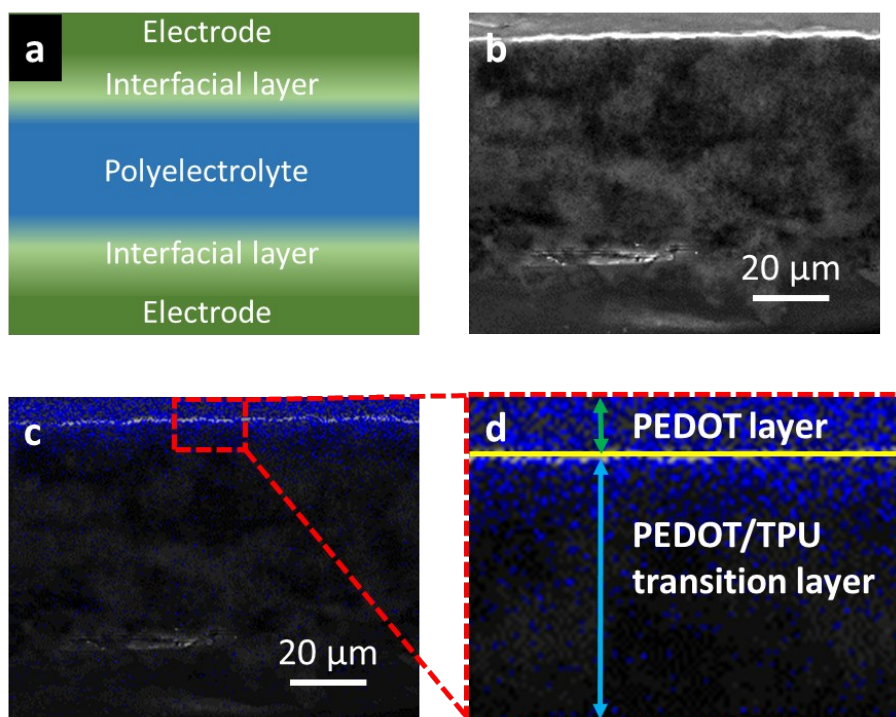


Fig. S9 (a) Schematic for cross section of supercapacitors prepared with interfacial polymerization method. (b, c) Cross-sectional SEM image and corresponding sulfur EDX mapping of the device. (d) Enlarged selected area of SEM image in (c).

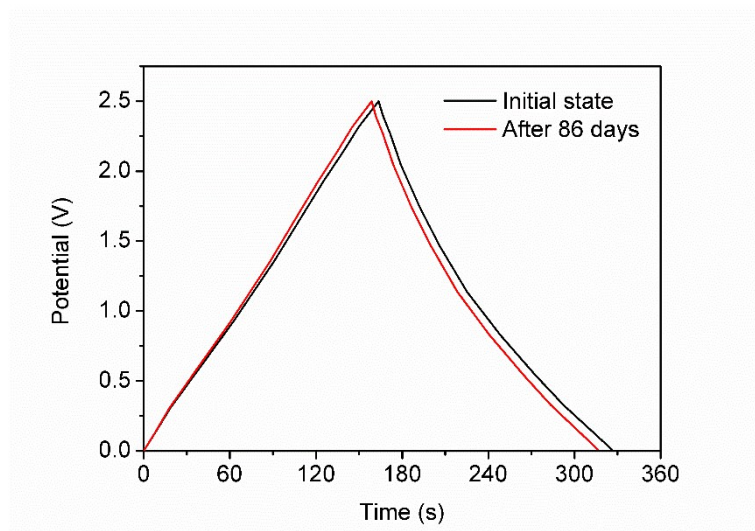


Fig. S10 Charge-discharge curves of the device at 1 A g^{-1} before and after keeping in air for 86 days.

References

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